Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/AU05/000523

International filing date: 12 April 2005 (12.04.2005)

Document type: Certified copy of priority document

Document details: Country/Office: AU
Number: 2004901907
Filing date: 13 April 2004 (13.04.2004)

Date of receipt at the International Bureau: 26 April 2005 (26.04.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)

PCT/AU2005/000523

Australian Government

Patent Office
Canberra

I, JANENE PEISKER, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2004901907 for a patent by MICROTECHNOLOGY CENTRE MANAGEMENT LIMITED as filed on 13 April 2004.

COMMONWEALTH OF AUSTRALIA
AUSTRALIA
PATENT OFFICE

WITNESS my hand this
Twenty-second day of April 2005

J. K. + C.

JANENE PEISKER
<u>TEAM LEADER EXAMINATION</u>
<u>SUPPORT AND SALES</u>

AUSTRALIA
Patents Act 1990

PROVISIONAL SPECIFICATION

200490 filed 13th April 2004

Invention Title : **Fabricated Strain sensor**

Applicant: **Microtechnology Centre Management Limited**
[A C N 088 163 366]

Inventors: **David Mainwaring**
Pandiyan Murugaraj

The invention is described in the following statement:

Fabricated Strain Sensor

This invention relates to strain sensors particularly micro strain sensors that can be easily fabricated and used for continual monitoring of structures subject to strain.

Background to the Invention

Polymeric strain gauges have been proposed.

WO 96 19758 discloses the preparation of pressure sensitive ink that can be used for the fabrication of pressure transducers such as strain gauges where the electrical resistance is indicative of the applied pressure. The ink has a composition of an elastic polymer and semiconductive nanoparticles uniformly dispersed in this polymer binder.

USA patent 55817944 discloses a strain sensor for a concrete structure containing conductive fibres.

USA patent 6079277 discloses a strain or stress sensor composed of a polymeric composite with a matrix of carbon filaments.

USA patent 6276214 discloses a strain sensor using a conductive particle – polymer complex. Carbon black is dispersed in an ethylene vinylacetate copolymer.

All these polymeric sensors are fabricated by preparing the conductive particles and then incorporating them in a polymer by solution or melt processing followed by film fabrication. This component is then pasted onto an insulating support and embedded onto the mechanical structure to be monitored. Electrical leads need to be connected to the sensor.

WO 0223962 discloses a laser irradiation process for forming conducting patterns on an insulating substrate.

JP 2000216521 discloses patterning of circuits for printed circuit boards by laser irradiation.

USA patent 5,900,443 deals with near surface treatment process produced by irradiation with high-energy particle beams. The process is preferably implemented with pulsed ion beams. The process alters the chemical and mechanical properties of the polymer surface. The ion beam radiation can have various effects such as cross-linking, pyrolysing, etching or ablation of the polymer in the treated areas. However there is no mention of conductivity in the polymer.

It is an object of this invention to develop a process with fewer fabrication steps to form easily mass produced strain sensors.

Brief description of the invention

To this end the present invention provides a method of forming a strain sensor from a polymeric film which includes the steps of selectively irradiating a surface of the polymer with high energy radiation to form conducting particles in the polymer to increase the electrical conductivity in selected portions of the surface.

This invention is partly predicated on the realization that the changes in the polymer, particularly the changes in interparticle gaps between conducting particles in the polymer will result in strain dependent electrical properties in the treated polymer.

A suitable class of polymers is polyimide which is commonly used in micro electronics devices.When polyimide is subjected to high energy ions (such as ^{12}C, ^{19}F, ^{32}S, ^{63}Cu , Xe, He, N, Ne, Kr etc.) via irradiation of the required fluence (of the order 10^{14} to 10^{17} ions/cm^2) , electrically conducting carbon particles are generated randomly in the polyimide matrix and thus a carbon-polyimide nanocomposite is formed instantly.

Three stages occur during this irradiation process:

- In the first localized polymer degradation producing dangling bonds and free radicals;
- In the second stage, gaseous products leaving the polymer with recombination of dangling bonds into some kind of disordered network of π-conjugated bonds and
- In the third stage, recrystallisation of the residual material in the irradiated region and the formation of metallic graphite clusters.

Such a composite is known to show enhanced electrical conductivity through variable range hopping / tunneling mechanisms. The electrical conductivity characteristics depends on the carbon particle density and inter-distance between the carbon particles which can be controlled by monitoring the irradiation parameters such as fluence, ion current and ion energy. The electrical conductivity

of the composite structure can be controlled in a wide range between an insulating region and metallic region (10^{-18} to 10^{2} S/cm)

These conducting carbon-polyimide composites are reported to have good stability and aging of these composites were not found to vary appreciably.

The electrical conductivity characteristics (temperature dependent/ deformation dependent /voltage dependent etc.) of such a system depends on, the carbon particle size , concentration of carbon particles, and the inter-particle distances.

In this invention deformation dependent changes in electrical properties of the carbon-polyimide nanocomposite film (which crucially depends on the changes in the inter-particle gaps occurring during deformation process) is exploited to achieve a strain sensor as an application of these films.

The concept of irradiation produced nanocomposite films for strain gauge devices provides a number of substantial product and fabrication process advantages:

1. Most importantly, the processing steps can be considerably reduced, no longer do nanoparticles have to be handled, stabilized, incorporated in polymer and dispersed in the thin films. Conducting particles are formed in-situ due to irradiation induced localized carbonization process. The particle size and its concentration can be controlled by monitoring the ion fluence and ion current.

2. A layer of defined thickness within a polymide film may be irradiated by controlling the radiation penetration depth leaving the remaining polyimide film unaffected with respect to its mechanical and electrical properties. This feature is not achievable by incorporating and mixing nanoparticles into the film material or precursors as traditionally carried out. Here is an advantage of having the conducting composite film and the insulating support in one and the same polyimide film

3. It is possible to form in-situ metal nanoparticles through metal compound and complex decomposition by irradiation, which through the selection of the irradiation parameters can occur without polymer decomposition and the formation of carbon nanoparticles. Mass transport mechanisms

within the film can be employed to control diffusion and growth in particle size

4. It is possible to micro-pattern strain sensors directly within the irradiation process forming the carbon or metal nanoparticles. Thus nanocomposite film formation and micro-patterning may become a single step fabrication process, for example, masked or spatially directed irradiation.

Detailed description of the invention

Figure 1 illustrates the fabrication steps used in one embodiment of this invention.

Typical ion beam irradiation processes which may be used in this invention have been reported in the literature

1. . Using ions of ^{12}C, ^{19}F, ^{32}S, ^{63}Cu etc. in the energy range of 30 to 60 MeV from a Van de Graaff Tandem Accelerator polyimide films were irradiated. Beam currents were limited 30 nA for S and Cu ions and 100nA for C and F ions. Thin 7.5 and 12.5μm polyimide films were used such that the ions were transmitted through the sample. The ions loose their energy to the polyimide matrix by electronic slowing down process along the trajectory. The conductivities achieved were up to 10^2 S/cm. (Salvetat et al., Phys. Rev. B 55 (1997) 6238).

2. The ions of Xe, He, N, Ne, Kr are used in the energy range 100 to 700keV and fluence in the range 10^{16} to 10^{17}. The conductivity achieved is 0.0005 to 360 S/cm (Davenas et al, UMR, CNRS (NIMB 32 (1988) 136)

   Other ions used by earlier authors are ionized B, Ne etc.

Also suitable for this invention are processes where an alternative irradiation source is used - UV (275-380nm KrF laser)

The intensity used is in the range 10-1000kW/cm^2 and conductivity achieved is as high as 25 S/cm. Results from three research groups are :

1. Feurer et al. (Applied Physics A: Solids and Surfaces, vol 56 (1993) 275) also reports on KrF laser induced conductivity. In their experiments, the typical laser parameters that the authors used were fluence of 40-80mJ/cm^{-2} at repetition rate of 5Hz. The critical number of shots, N_c as well as the

order of magnitude of conductivity, reached after approximately after 1000 shots, both depend on the fluence. For a fluence of about 40mJ/cm^2, N_c is 270; the saturation conductivity reaches above 1000 shots to about 0.1 S/cm and 10 S/cm for 80mJ/cm^2 fluence. Excimer laser is capable of permanently changing the resistivity of the polyimide by 16 orders of magnitude.

2. Continuous UV (275-363nm) focused on the spot such that its intensity 10-100kW/cm^2 can write conducting pattern at speeds up to 90cm/s on the surface of a film of polyimide and a conductivity of 20-25 S/cm is reached (lines as narrow as 15 microns or as uniform areas of upto 2 cm^2 can be produced. Conductivities did not degrade for months (Synthetic Metals 66 (1994) 301, Chem. Mater. 6 (1994) 888 UV tech Associates in New York, Srinivasan et al)
3. 1993 paper by Phillips et al. (App. Phys. Lett. 62 (1993) 2572) claims to be the first paper to make permenant electrically conducting periodic structures with sub micron spatial resolution. KrF laser (248nm) is used in this work. (Laser irradiation of polyimide above a certain threshold fluence (~20mJ/cm2) produces localized clusters of carbon rich material with average diameters around 10nm. After a number of shots, these clusters become interconnected, and the conductivity undergoes metal insulator percolative phase transition. Bulk sample was irradiated with a uniform fluence of 40 mJ/cm2 and 2100 laser shots. The resistance measured was 310kiloOhms corresponding to 15 ohm cm micrometer)

Other types of irradiation sources which may be used are:

Gamma rays 10^7 to 10^9 .
Protons 7.7MeV at 1 – 10^4 Gy/s
Electron beam 900keV

The process steps required for the fabrication of strain sensor through the currently proposed process are illustrated in figure 1:

1. Fabrication of highly homogeneous thick polyimide films (15-50microns) /or procurement of commercially available prefabricated films.
2. Design of suitable mask to selectively irradiate the polyimide

3. Irradiate the film with predetermined fluence and ion current values so that carbonization occurs only on the unmasked area and to the depth determined by the fluence, energy and ion current.
4. The conducting tracks for electrode formation also can be achieved through the same irradiation process with different set of fluence and ion current values.
5. This can be directly laid on to the mechanical structure under investigation.

Hence to fabricate a strain sensor on a polyimide film, the top surface of the film should be subjected to irradiation process through suitable mask for the formation of the conducting strain sensor pattern. Control of the irradiation parameters will allow the bottom portion of the polyimide film unaffected by the radiation. This portion of the film would act as a supporting base. This enables direct embedding of the strain sensor on to the mechanical structure that has to be studied.

The following are examples of specific irradiation parameters that produce specific values of conductivity.

1. Terai and Kobayashi (NIMB 166-167 (2000) 627)

PI film used:	14 µm thick cut into 2 x 2 cm squares and only 1cm by 1cm area was irradiated using an aluminium mask
Irradiation Parameters:	Ni^{3+} accelerated to 4MeV and the beam was scanned so that the fluence was same for all the irradiated area; Irradiation fluence was from 3.5 10^{12} to 1.0 x 10^{16} cm^{-2} and the current density 100 µA cm^{-2} under 10^{-5} Pa. The temperature of the rear side of the specimen was less than 50°C
Electrical Conductivity:	Their data shows that at a typical fluence of $10^{15} cm^{-2}$, a sheet resistance of 100-1000 ohms is achieved.
Depth profile of Ni atoms:	The mean ion range in the polyimide specimen was 3 µm

2. Davenas, Boiteux and Xu, NIMB 32 (1988) 136

PI-Films Used:	No details

Irradiation Parameters: Xe^+ beam of current density 0.5μA/cm^2 at different energies between 1.5 MeV and 500keV and fluence used in the order or 10^{15} to 10^{17} Xe^+/cm^2

Electrical Conductivity: The sheet resistance obtained was between 50 and 10000 ohms. for 0.5MeV, 10000 ohms is obtained (10^{17} Xe^+/cm^2); for 0.7MeV, 100 ohms is obtained (10^{17} Xe^+/cm^2)

3. De Bonis, Bearzotti and Marletta NIMB 151 (1999) 101

PI films used: 1.3 micron films were spin coated on 5 inch wafer

Irradiation Parameters: Irradiated with 600keV Ar^+ ions from 10^{14} to 10^{15} in a high voltage ion implanter. The ion current was below 100nA Projected range of ion was 0.7 μm.

Electrical Conductivity: Current voltage measurements were performed 380 ohm were obtained for sample when irradiated with 10^{15} ions per cm^{-2}

4. Feurer, Sauerbrey, Smayling, and Story, App. Phys. A 56 (1993) 275

PI Films: Kapton foils of 50 microns thick were used

Irradiation Parameters: KrF laser is used for irradiation process. Irradiated with an injection controlled KrF which emitted 30ns (FWHM) pulses with a repetition rate between 0.5 and 8 Hz, in both directions. The sample was also rotated at a speed of 10 revolutions per minute.

Depth of Conducting Layer: 50 nm thick conducting layer was formed

Electrical conductivity: Above a fluence threshold of $20mJcm^{-2}$, the electrical conductivity exhibits insulator–conductor transition after a critical number of shots. With 40 mJ cm^{-2} at a laser repetition rate of 5 Hz, a conductivity value of 10^{-4} S/cm (resistivity of the order 10000 ohm-cm) is reached after 1000 shots.

This newly proposed method simplifies the strain sensor fabrication process since in the currently known fabrication processes, the conducting composite strain sensor has to be rested on an insulating support before it can be imbedded onto the structure whose deformation characteristic is to be investigated.

CLAIMS

1. A method of forming a strain sensor from a polymeric film which includes the steps of selectively irradiating a surface of the polymer with high energy radiation to change the composition of the polymer and increase the electrical conductivity in selected portions of the surface.
2. A method as claimed in claim 1 in which the high energy radiation carbonizes the polymer to form conductive particles in the polymer.
3. A method as claimed in claim 1 in which high energy ions impinge on a polymer film containing precursor metal compounds, such that decomposition of the precursor leads to nucleation of conducting metal particles.
4. A method as claimed in any preceding claim in which the polymer is a polyimide.
5. A strain sensor made by the method of any preceding claim.

ABSTRACT

A method of forming a strain sensor from a polymeric film includes the steps of selectively irradiating a surface of the polymer with high energy radiation to change the composition of the polymer and increase the electrical conductivity in selected portions of the surface. The radiation can create carbonized particles or metallic particles within the polymer and the changes in interparticle gaps between conducting particles in the polymer will result in strain dependent electrical properties in the treated polymer.

Carbon Dispersed PI-Thin Film Strain Sensor Using Ion Beam Irradiation

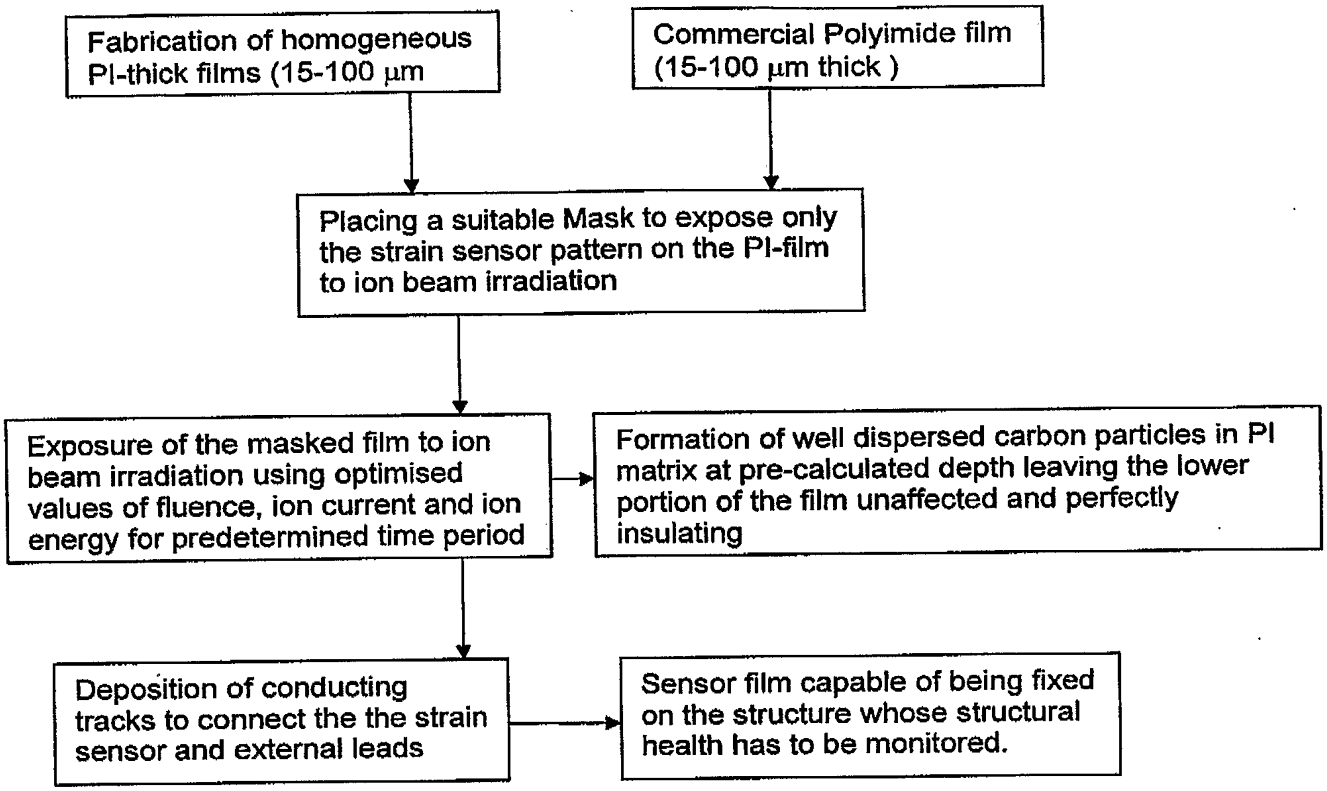

FIGURE 1